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(54) Title: DYEABLE POLYOLEFIN COMPOSITIONS AND METHOD (57) Abstract Compositions of ethylene/alkyl acrylate blended or grafted with polypropylene are dyeable with disperse or cationic dyes. Compositions of polyolefin, a small amount of polyester and polar material selected from ethylene/alkyl acrylate, maleic anhydride and acrylic acid are also dyeable. A hydrophilic modifier of a monoglyceride and a salt of a linear alkyl phosphate may be included. The compositions are fiber forming.		

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DYEABLE POLYOLEFIN COMPOSITIONS AND METHOD

Field of the Invention

The present invention relates to an improved dyeable polyolefin composition and to a process for dyeing fibers and nonwoven materials formed from this composition. More particularly, the invention is directed to a disperse-dyeable fiber composition comprising polypropylene, polyester, and a polar material such as ethylene copolymer. The invention is additionally directed to a formulation and process that will allow the use of cationic dyes for polyolefin-based compositions.

Background of the Invention

Polyolefins are hydrophobic and difficult to dye in that they lack dye sites to which dye molecules may become attached. One approach to color polyolefin fibers has been to add colored inorganic salts or stable organometallic pigments to polymer melts prior to fiber spinning. Nonvolatile acids or bases, or materials such as polyethylene oxides or metal salts, have been added to polymers prior to fiber formation to increase the affinity of the fiber for disperse, cationic, acid, or mordant dyes. Polyolefin fibers may be grafted chemically with appropriate monomers after fiber formation to improve dyeability. *Textile Fibers, Dyes, Finishes, and Processes: A Concise Guide*, Howard L. Needles, Noyes Publications, 1986, p. 191.

Efforts to impart acid dyeability to polyolefins, and particularly polypropylene, include the use of nitrogen-based polymer additives. For example, in U.S. Patent No. 3,361,843, various incompatible, nitrogen-based polymers are added to polypropylene, given a treatment with high concentrations of acidic chemical reagents, and then dyed in an acid dye bath. According to U.S. Patent No. 3,653,803, dyeing of the polypropylene fiber is somewhat improved by the method of U.S. Patent No. 3,361,843, but processing of the fiber is difficult due to the incompatible polymer, the dye fastness properties not being reliably reproducible, and tinctorial strengths not being commercially sufficient. In U.S. Patent Nos. 3,395,198 and 3,653,803, various compatible nitrogen-containing copolymers of ethylene and

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an aminoalkyl acrylate compound are disclosed that, when blended with polyolefins, render fibers formed from the blend acid dyeable. In U.S. Patent No. 5,017,658, a fiber finishing agent is used in melt spinning dyeable polypropylene fibers obtained by blending a copolymer of an ethylene aminoalkyl acrylate with polypropylene.

5 In U.S. Patent No. 4,557,958, a blend of 70% by weight polypropylene homopolymer and 30% by weight ethylene-methylacrylate copolymer is applied to a fabric of woven polyolefin as a coating stripe to prevent fraying of the fabric when the fabric is cut. In U.S. Patent No. 4,853,290, a blend of ethylene-acrylic acid copolymer and ethylene-methylacrylate copolymer is coextruded onto a polypropylene
10 film to serve as an adhesive or tie layer to a second polymer.

In U.S. Patent No. 4,782,110, melt processible multiphase thermoplastic compositions are described that can be formed into various shapes by compression molding, injection molding, blow molding, and extrusion. The composition comprises a blend of crystalline polyolefin resin forming the continuous phase of the
15 composition and a cross-linked elastomer of an ethylene alkyl acrylate copolymer forming the discontinuous phase of a composition. The elastomer consists of units derived from ethylene, an alkyl ester of acrylic acid wherein the alkyl group contains 1 to 6 carbon atoms, and a monoalkyl ester of 1,4-butenedioic acid wherein the alkyl group contains 1 to 6 carbon atoms.

20 U.S. Patent Nos. 3,373,222 and 3,373,223 disclose polymeric blends comprising polyolefin resin, polyamide resin, and either a carboxylated polyethylene, an ethylene-acrylic, or a methacrylic acid copolymer. Homogeneous polymeric blends have utility in the preparation of films useful in the packaging industry and in the preparation of plastic bottles and other containers that require a high degree of
25 impermeability.

U.S. Patent No. 3,454,215 discloses a dyeable polypropylene composition comprising a polyamide and ethylene copolymer. The composition may consist of a uniform admixture of polypropylene, a low molecular weight thermoplastic unreactive polyamide, and an additional polymer selected from a group consisting of copolymers
30 of ethylene and an ethylenically unsaturated ester of a saturated fatty acid or a hydrolyzed product of such copolymers. U.K. Patent Specification No. 998,439 also discloses a thermoplastic composition comprising polyamides and olefin copolymers.

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U.S. Patent No. 5,017,658 discloses a dyeable polypropylene composition including a copolymer of an aminoalkyl acrylate with polypropylene. U.S. Patent No. 4,368,295 discloses a film produced by a melt extrusion process made from compositions containing an olefin polymer, a linear polyester, and a carboxylated polyolefin. U.S. Patent No. 4,174,743 discloses split-fiber, thread, and film products comprising polypropylene and one or more polyesters and/or polyamides.

A chapter entitled "Dyeing of Polypropylene Fibers" in *Polypropylene Fibers, Science and Technology* by Mike Ahmed provides a comprehensive study of the technology involved in dyeing polypropylene fibers in the mid 1950s to the 1980s. Section IV.1 regarding mordant-dyeable fibers discusses problems relating to light fastness, wash fastness, and crock fastness of certain dyes. The study concludes that the fastness properties of disperse-dyeable polypropylene fibers are generally unacceptable to the textile trade.

An article entitled "Surface Dyeable Modified PP BCF Yarns" in *Chemiefasern/Textilindustrie*, Vol. 41/93, October 1991 discusses adding a modifier to PP BCF yarn. A brochure entitled *Polymer Compounding* by Eastman Chemical Products, Inc. discusses Epolene E-43 wax as a compatibilizer for nylon/polypropylene composites. An articles entitled "Morphological and Mechanical Properties of Extruded Polypropylene/Nylon-6 Blends" by Wan Gheluwe et al. discusses nylon and polypropylene blends using Zytel 211 as a compatibilizer. An article entitled "New Functional Materials for Absorbent Products" by Dr. Suzuki in *The New Nonwoven World*, Fall 1993 discusses new polypropylene materials for absorbent products.

In an article entitled "Polymer Morphology on the Dyeing Properties of Synthetic Fibers," Keith Silkstone reviews some of the prior art efforts conducted with regard to proposing morphological changes in the fiber production for marginal dye uptakes in polypropylene. Other relevant articles are "Dyeing Synthetic Fibers," H.E. Schroeder, *C&EN*, Sept. 10, 1956; "Dyes for Hydrophobic Fibers," H.E. Schroeder et al., *Textile Research Journal*, Vol. 28, April 1957; and "The Influence of Polymer Morphology on the Dyeing Properties of Synthetic Fibers," Keith Silkstone, *Rev. Prog. Coloration*, Vol. 12, 1982.

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The need exists for improved polyolefin compositions and materials that will be commercially dyeable with a broad range of dyes. A particular need exists for polypropylene-based compositions that can be used to manufacture fibers that are spinnable and may be formed into fabric sheets including nonwoven fibers.

5 Summary of the Invention

According to the present invention, there are provided novel compositions and articles of polyolefins that are more dyeable, novel methods of dyeing polyolefin articles, and novel shaped dyed articles, including novel dyed polypropylene fibers, produced by such processes.

10 A novel polyolefin fiber comprises about 99% to 85% by weight of a polyolefin and a selected amount of an ethylene copolymer comprising about 70 to 82% by weight ethylene and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl has 1 to 4 carbon atoms, said composition containing 0.2 to 3.0% alkyl
15 acrylate by weight the sum of the polypropylene and ethylene copolymer, wherein at least a portion of said copolymer is grafted onto said polyolefin and an effective amount of a disperse dye diffused into the polypropylene to produce a colored fiber. A hydrophilic modifier may be included that comprises a monoglyceride and a long chain hydrocarbon with a hydrophilic group.

20 A novel process for forming polypropylene-based fibers comprises (a) combining polypropylene with a selected amount of an ethylene copolymer of about 70 to 82% by weight ethylene and about 30 to 18% by weight of an ethylene alkyl acrylate wherein the alkyl group has 1 to 4 carbon atoms to form a composition; (b) extruding the composition into fibers; and (c) exposing the fibers to a selected disperse dye bath containing a disperse dye, either for dyeing or printing.

25 A novel polyolefin fiber comprises about 99 to 70% by weight polypropylene; a fiber grade polyester of from about 0.1 to 15% by weight; a selected amount of a polar group material, such as an ethylene copolymer, a maleic anhydride, or an acrylic acid; and a hydrophilic modifier comprising a monoglyceride and a salt of a linear alkyl. The polyester may be compounded with the polypropylene/polar group
30 material/hydrophilic modifier matrix. The ethylene copolymer may comprise about 70 to 82% by weight ethylene and about 30 to 18% by weight of an alkyl acrylate,

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wherein the alkyl has 1 to 4 carbon atoms, said alkyl acrylate present in an amount of 0.2 to 3.0% by weight. The hydrophilic modifier may comprise a fused combination of a monoglyceride and a linear alkyl phosphate and provides additional compatibilization of the polypropylene and polyester. This modifier may be present
5 in an amount of from 0.1 to 2% by weight, and preferably between 0.4 and 1.0% by weight; the sum of the polypropylene, polyester and ethylene copolymer.

A novel process for dyeing shaped articles based on a polyolefin comprises (a) forming into a fiber a composition of about 99 to 70% by weight of a polyolefin and a selected amount of an ethylene copolymer comprising about 70 to 82% by weight
10 ethylene and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl has one to four carbon atoms; and (b) exposing the fiber to a disperse dye.

A novel process for dyeing fibers based on polypropylene comprises (a) combining polypropylene with a selected amount of an ethylene copolymer of about 70 to 82% by weight ethylene and about 30 to 18% by weight of an ethylene alkyl
15 acrylate wherein the alkyl group has one to four carbon atoms, to form a composition; (b) extruding the composition into fibers; and (c) exposing the fibers to a selected dye bath.

A novel process for forming fibers based on polypropylene comprises combining isotactic polypropylene, polyester, a polar group material, and a selected
20 hydrophilic modifier. The polar group material may be ethylene copolymer of about 70 to 82% by weight ethylene and about 30 to 18% by weight of an ethylene alkyl acrylate wherein the alkyl group has 1 to 4 carbon atoms. Alternatively, the polar group material may be a maleic anhydride or an acrylic acid. The hydrophilic modifier may be present in an amount between 0.1 and 2.0% by weight, and
25 preferably between 0.4 and 1.0% by weight, the sum of the polypropylene, polyester, and ethylene copolymer. The polyester or copolyester thus has excellent compatibility to the modified polypropylene. Polyester may be incorporated at a very minute level of about 0.1% by weight up to about 15% by weight. To obtain an acceptable level of dyeability with a high exhaust level and subsequent high light
30 fastness, a desired level of polyester may be between 1 to 10% by weight, with an optimum level at about 3% by weight.

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The disperse dye allows for the cost-effective production of fibers that preferably have good light fastness and, in at least some instances, good wash fastness, and good crocking (bleeding) properties. Generally, the dye will have a comparatively high mass to polarity ratio and will be only slightly polar. The rate of dyeing is inversely proportional to the mass of the dye and directly proportional to the linearity and absence of bulky side chains. A dye having low solubility in water and high solubility in fiber is preferred. Dyes generally intended for dyeing acetate fibers or polyester fibers are likely candidates. An open amorphous fiber structure is also preferred. Based on the work that was conducted on several standard dyes, this unique composition exhibits tremendous exhaust characteristics with an acceptable level of light/wash fastness and crock characteristics.

The polyolefin in these compositions and processes preferably is isotactic polypropylene. In the processes, the composition may be a blend or one in which at least a portion of the ethylene copolymer is grafted onto said polyolefin. The ethylene copolymer in the compositions include ethylene methyl acrylate, ethylene ethyl acrylate, and ethylene butyl acrylate.

It is an object of the present invention to provide an improved inert hydrophobic polyolefin-containing composition with desired dyeability and wettability characteristics. It is a further object of the present invention to provide an improved polyolefin-containing web comprised of fibers, or a nonwoven or fibrillated film suitable as cover stock for various sanitary products. Still another object is to obtain and retain high hydrophilicity and liquid strike-through properties in a strong, well-bonded, nonwoven hydrophobic material, including continuous and/or staple fibers utilizing polyolefin components.

It is a significant feature of this invention that the polypropylene-based material may be used to form fibers having applications for either woven materials or nonwoven materials, and that the fibers are spinnable at commercially acceptable rates. Yet another feature of the invention is that a polypropylene-based material may be efficiently modified to form a material having a wettability contact angle of less than about 80°.

An advantage of the invention is that the wettable polyolefin material according to this invention is more easily dyeable than prior art polyolefin fiber

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materials. These and further objects, features, and advantages of the present invention will become apparent from the following detailed description.

Detailed Description of the Invention

Polyolefins usable in accordance with this process are crystalline polyethylene, polypropylene, or copolymers thereof having melt indices in the range of from about 0.1 to about 80 g/10 min. The most important polyolefin for use in formation of fibers at this time is isotactic polypropylene, which is commercially available from many sources. The polypropylene can contain the usual thermal, oxidative, and ultraviolet light stabilizers.

The fiber-forming composition may comprise polypropylene and a copolymer of ethylene and an alkyl acrylate having 2 to 30% by weight, suitably 2 to 15%, preferably 4 to 10%, most preferably about 7%. In accordance with this invention, the copolymer of ethylene and an alkyl acrylate may be grafted onto the polypropylene. The composition may alternatively include a blended polypropylene/copolymer mixture, or both grafted and blended ethylene alkyl acrylate copolymer. An advantage of the ethylene alkyl acrylate copolymer is that it is both thermoplastic and compatible with polypropylene so that processing difficulties are minimized or prevented. By the term "compatible" is meant that the copolymer does not separate into discrete particles in the polypropylene composition that are observable under an optical microscope at a magnification of times 250-500. The grafted version of polypropylene offers an excellent bridge for optionally adhering with the polyester or copolyester.

The ethylene copolymer comprising ethylene and an alkyl acrylate in the compositions used in this invention include ethylene methyl acrylate, ethylene ethyl acrylate, and ethylene butyl acrylate. Ethylene methyl acrylate copolymer ("EMA") alone or in blends has been used in film, extrusion coating, sheet, molding, tubing, profile extrusion, and coextrusion areas. Compared to low density polyethylene homopolymer, it has a lower softening temperature (138°F), a reduced flexural modulus, and improved environmental stress crack resistance. Ethylene copolymer has been disclosed for use as a blending component with low density polyethylene, polypropylene, polyester, and polycarbonate to improve impact strength and

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toughness, increase heat seal response and promote adhesion, reduce stiffness, and increase the surface coefficient of friction. *Modern Plastics*, Mid-October Encyclopedia Issue, 1991, pp. 71-72.

Ethylene ethyl acrylate copolymer ("EEA") resins are tough, flexible
5 copolymers that have found application in hoses and tubings, gasketing, disposable examination gloves, and balloons. EEA has also been used for hot melt adhesives. As the ethylacrylate content of EEA increases, the copolymers become more flexible, tougher, and more resilient. The polarity of high ethylacrylate resins may enhance surface acceptance of inks and provide adhesive properties. Ethylene butyl acrylate
10 ("EBA") is used for low melt-index films. It produces a tough film at low temperatures and is employed mainly in the packaging of frozen foods.

Particularly preferred copolymers are the ethylene methyl acrylate random copolymers of ethylene and methylacrylate and the ethylene ethyl acrylate random copolymers of ethylene and ethylacrylate. The EMA copolymers preferably contain
15 about 20 to 24%, and preferably about 20%, by weight methylacrylate. The EEA copolymers preferably contain about 15 to 30% by weight of the ethylacrylate moiety. These copolymers have a melt index of 1 to 20, preferably about 18, and have a thermal stability such that when the temperature is raised at 10°C/min., under flowing nitrogen, less than 0.75% of the copolymer weight is lost at 300°C.

20 It is a critical feature of the present invention that the amount of alkyl acrylate in the polypropylene ethylene alkyl acrylate copolymer be present in an amount between 0.2 to 3.0% by weight, and preferably between 0.5 and 2.4% by weight, in order to produce a textile fiber having commercially acceptable processing characteristics. If the amount of alkyl acrylate component is increased above 3.0%,
25 a textile fiber produced therefrom loses its necessary polypropylene characteristics, degrades during high-speed fiber processing, and produces a final fiber with unacceptably low tenacity (less than about 1.5 g/denier) and excessive elongation and with significantly different melt characteristics to be commercially unacceptable. For example, carpet made from fibers having an alkyl acrylate component between 3.0
30 and 5.0% melts excessively upon exposure to flame as compared to conventional polypropylene carpet to the point that it dramatically fails a standard "pill test" for flame resistance while standard polypropylene passes. Further, at an alkyl acrylate

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content above 2.4%, the fiber fuses together on the heated drawing rolls and is basically unspinnable on modern commercial scale equipment. These subtle, yet commercially critical, limitations were complete unexpected.

5 An alkyl acrylate component of less than 0.2% produces a fiber with insufficient polarity performance character to impart a desired dyeability to accept a desired even, deep color. Accordingly, the maximum amount of alkyl acrylate component is preferred, subject to acceptable fiber production and performance character. The more preferred alkyl acrylate component is between 0.5 to 2.4% by weight for polypropylene compositions which do not include polyester, with 1.0 to 10 1.5% being most preferred for polypropylene/polyester compositions. Polypropylene without the grafting process does not form continuous or bulk-continuous filaments with polyester or copolyester. The degree of compatibilization to enhance the processibility can be augmented by incorporating the hydrophilic modifier, such as a monoglyceride and a long chain hydrocarbon with a hydrophilic group.

15 It is understood that polymer additives, such as thermal, oxidative, and ultraviolet light stabilizers, which are typically found in fiber-forming polymer compositions, may be added without departing from the present invention. The percent by weight values given in this application are expressed as a percent by weight of the composition which includes a polyolefin, such as polypropylene, and 20 a polar material, such as an alkyl acrylate copolymer, and preferably both a hydrophilic modifier and polyester. The percent values stated for these materials should thus uniformly combine to 100%. Other additives may be included to dilute the polyolefin composition. If such additives are included in the composition, the ratio of polyolefin to polar material would remain constant, and the total percent 25 values of all materials, including additives, would then exceed 100%. For example, if nylon were used in the composition which did not include polyester, the percent values of the polypropylene, copolymer and hydrophilic modifier would not change, and would still total 100%.

30 The ethylene copolymers utilized in the present invention contain at least 70% ethylene, with the alkyl acrylate component present between 2 to 30%, typically between 10 to 24%, depending upon the selected alkyl acrylate. Depending upon the amount of alkyl acrylate component present in the ethylene copolymer, the ratio

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of ethylene copolymer to polypropylene can be easily adjusted to maintain the proper amount of alkyl acrylate in the final product. It is also important that the amount of ethylene contributed by the ethylene copolymer be maintained below 10%. Accordingly, it is preferred that the higher the percentage of alkyl acrylate in the copolymer, the easier it is to obtain the proper balance of components. By way of example, a mixture of 93% polypropylene and 7% ethylene methyl acrylate having a 20% methyl acrylate component produces a polypropylene/ethylene methyl acrylate copolymer composition having a methyl acrylate component of about 1.4%. Similarly, a 3% addition of the same ethylene methyl acrylate copolymer produces a methyl acrylate component of 0.6%.

The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated.

Example 1

A polypropylene alloy composition containing 90% by weight of a commercial fiber grade of isotactic polypropylene having a melt flow rate of 18 (ASTM D-1238-89, 230°C, 2.16 lbs) and containing thermal, oxidative and ultraviolet light stabilizers and 10% by weight of a copolymer of ethylene methylacrylate is prepared by first dry mixing the polymers and then melt blending the mix in a 40 mm Berstorff extruder at 246°C. The ethylene copolymer contains 24% by weight of the methylacrylate comonomer, and has a melt index of 18 (ASTM D-1238-89, 190°C, 2.16 lbs). The resulting homogeneous, compatible polymer blend is cut into nibs after water-quenching, which are then fed to a melt spinning apparatus and 50-60 denier per filament fiber is spun at 230-245°C. A mineral-oil based finish containing anionic surfactants is applied to the fiber bundle after spinning, but before drawing. The fibers are drawn times three to give a final denier of 18-20 per filament. Specimens of the fibers are knitted on a knitting machine to produce a tubular knit fabric. Samples of the fabric are dyed according to the procedure given below.

Dye procedure steps involving a scour, dye, and reduction clearing operation were used, as explained hereafter. In the scour step, the sample was rinsed in cold water for 5 minutes and the bath changed. The sample was introduced in a new bath of 0.5 g/l Keirlon TX-199 wetting agent/detergent and 0.25 g/l of soda ash, then

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heated to 160°F and held for 10 minutes. After cooling to 100°F, the sample was rinsed.

In the dye step, the dye bath was prepared as follows: 1% dye, 1% Triton X-100 (surfactant), 1% Synthrapal LFP (disperse leveling agent). The pH was brought to 5.5 with acetic acid and the bath heated to 120°C at 2.5°C per minute. The bath was held at that temperature for 30 minutes, then cooled to 40°C at 3°C per minute. The sample was rinsed warm, extracted, and dried. Optionally, for good fastness properties an additional step, namely, reductive clearing/stripping, may be carried out as follows.

In the reduction clearing step, wash dyed samples are placed in a series of tanks: first tank, wet out with Triton X-100; second, third, and fourth tanks, reductive clearing at 70°C with 8 g/l of sodium hydroxide at 32% concentration, 4 g/l sodium hydrosulfite for a total of 30 seconds. Rinse occurs in the fifth tank, and the sample is neutralized with acetic acid in the sixth tank. This process of reductive clearing ensures the removal of surface adhered dyes and in general produces better fastness results.

Example 2

A polypropylene graft composition containing 90% by weight of a commercial fiber grade of isotactic polypropylene having a melt flow rate of 4 (ASTM D-1238-89, 230°C, 2.16 lbs) and 10% by weight of a grafted copolymer of ethylene methylacrylate (and containing thermal, oxidative and ultraviolet light stabilizers) is prepared by first dry mixing the polymers and then melt blending the mix in a 40 mm Berstorff extruder at 246°C in the presence of sufficient free radical initiator peroxide, specifically, 2,5-dimethyl-2,5-di(tertiary-butyl peroxy)hexane, to visbreak the composition to a product melt flow rate of 18. The ethylene copolymer contains 24% by weight of the methylacrylate comonomer, and has a melt index of 18 (ASTM D-1238-89, 190°C, 2.16 lbs). The resulting homogeneous, compatible polymer blend is cut into nibs after water-quenching, which are then fed to a melt spinning apparatus and 50-60 denier per filament fiber is spun at 230 - 245°C. A mineral-oil based finish containing anionic surfactants is applied to the fiber bundle after spinning, but before drawing. The fibers are drawn times three to give a final denier of 18-20 per

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filament. Specimens of the fibers are knitted on a knitting machine to produce a tubular knit fabric. Samples of the fabric are dyed according to the procedure given in Example 1.

Example 3

5 A polypropylene graft composition containing 90% by weight of a commercial fiber grade of isotactic polypropylene having a melt flow rate of 4 (ASTM D-1238-89, 230°C, 2.16 lbs) (and containing thermal, oxidative and ultraviolet light stabilizers) and 10% by weight of an alloyed and grafted copolymer of ethylene methylacrylate is prepared by first dry mixing the polymers and then melt blending
10 the mix in a 40 mm Berstorff extruder at 246°C in the presence of sufficient free radical initiator peroxide, specifically 2,5-dimethyl-2,5-di(tertiary-butyl peroxy)hexane, to visbreak the composition to a product melt flow rate of 35. The ethylene copolymer contains 24% by weight of the methylacrylate comonomer, and has a melt index of 18 (ASTM D-1238-89, 190°C, 2.16 lbs). The resulting
15 homogeneous, compatible polymer blend is cut into ribs after water-quenching, which are then fed to a melt spinning apparatus and 4 denier per filament fiber spun in a partially oriented yard (poy) operation at a take-up speed of 3,000 rpm, and subsequently false twist textured to 2.0 to 2.5 dpf fibers. Specimens of the fibers are knitted on a knitting machine to produce a tubular knit fabric.

20 A series of samples of polymer made as described in Examples 2 & 3 and were evaluated with a series of disperse dyes according to the dye procedure of Example 1. The results are set forth in Table I. No appreciable difference was detected with respect to dyeing characteristics between Example 2 and Example 3 samples. Table I lists dyes that are suitable for dyeing fibers according to the present
25 invention. Light fastness, and crock fastness tests were also performed on yarns at 2-20 deniers per filament.

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TABLE I
DYE EXHAUSTION

Dye Exhaustion					
5	Experimented Dye Type Disperse Dyes at 1% Concentration	Light Xenon AATCC 16E- 40 hours	Crock Fastness AATCC 8-1985		Exhaust/ Yield
			Dry	Wet	
10	Disperse Blue 361				4
	Disperse Violet 28	4-5			3-4
	Disperse Blue 77				3-4
	Disperse Yellow 23	5	5	5	4-5
	Disperse Yellow 54	4	5	5	4
	Disperse Yellow 86	4	4-5	4-5	4
	Disperse Yellow 232	1	4-5	4-5	3-4
15	Disperse Yellow 3	5	5	5	3-4
	Disperse Blue 35	4	4-5	4-5	3-4
	Disperse Blue 87	4	5	5	4
	Disperse Blue 291	3-4	5	5	4-5
	Disperse Blue 354	1	4	4	4-5
	Disperse Blue 60	5	3-4	3-4	4
	Disperse Blue 118	4-5	4-5	4-5	3-4
20	Disperse Blue 183	1			5
	Disperse Red 60	4-5	3-4	3-4	4-5
	Disperse Yellow 64	5			4-5
	Disperse Red 167	3-4	4-5	4-5	3-4
	Disperse Red 73	1	4	4	4
	Disperse Red 127	3			3-4
	Intrawhite FWA	4-5	5	5	4-5
25	Disperse Green 9	1	4-5	4-5	4-5
	Disperse Blue 79	1	4	4	3-4

FASTNESS RATING

- 5 - No Change
4 - Slight Change
3 - Noticeable Change
2 - Significant Change
1 - Severe Change

EXHAUST RATING:

- 5 - Total Exhaust
4 - Good Exhaust
3 - Moderate Exhaust
2 - Poor Exhaust
1 - Light Staining

Dye exhaust or the extent to which the textile depletes a dye bath has been primarily used as the basis for determining the dyeability of the polyolefin. Other performance properties, such as light fastness, wash fastness, and crock fastness, are more a function of many other variables, such as the conditions of dyeing, the auxiliaries used in dyeing, and, in general, the dye procedure and the after-treatment.

Consistent with the Gray Scale Grading System devised by the AATCC, a scale of 1 to 5 is used, with 5 being a near total exhaustion of the dyestuff from the dye bath to the substrate and 1 being merely a staining of the substrate, almost all dyestuff remaining in the bath. All other grades between 5 and 1, including the intermediates such as 3-4, are based upon a linear scale of dye exhaust from the bath to the substrate. While a rating of 5 would be the most preferred, for operational purposes a rating of 3-4 or above is acceptable as a standard for a polymer fiber to be considered "dyeable" with a particular dye.

Those skilled in the art will appreciate that in most commercial applications, the disperse dyestuff will be a mixture of one or more selected dyes. The concentration of the selected disperse dye or dyes should be at least 0.1% to obtain the significant benefits of the invention. There is a current trend for blends of dyes to be used which optimize different characteristics of specific dyes for maximum performance. Carpets made from disperse dyed fibers from this polymer exhibited excellent resistance to bleaching. In a bleach test it was found a typical 10% solution did not produce a change in color, whereas a 100% solution produced only a significant to moderate change in color.

Carpet samples made from the subject polymer and disperse dye are stain resistance as per the carpet industry's standard Kool-Aid test. On a scale of 1 to 10, the samples scored an absolute 10, indicating no stain on tested samples. Generally

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speaking, dye results indicate that the grafted version of the present invention taught in Example 2 and Example 3 show a slightly better performance than the blended copolymer version of Example 1.

The present invention is particularly useful with fibers, and fibers of various deniers can be adequately wetted both in the form of fibers or nonwoven webs made from these fibers. Round or lobed fibers are for apparel, upholstery, and carpet face yarn uses and can have a denier of about 1 to 60 without encountering dyeing problems by the present technique. These fibers can also be used in production of other articles, such as decorated ribbons or nonwoven textiles. The tape fibers are generally used for carpet backing and are of heavier denier, i.e., about 500 to 1500 denier. Fibrillated film fibers are used to cordage carpet face yarn or upholstery.

For fibers to be fully penetrated by dye, the spinning and drawing processes should be conducted in a manner to produce a fiber with a uniform structure through its cross-section, i.e., minimal sheath/core structural differences. On the other hand, greater economy of dye used in dyeable carpet backing made from woven tapes can be obtained if such tapes do possess a sheath/core structure. In these sheath/core structures, the sheath is dyeable, while the core exhibits very little dye pick-up. Thus, less dye is used to dye a backing that is made up from such fibers.

After spinning of the fibers, but before drawing, a spin finish can be applied to the fibers. If such a material is used, it may be anionic, but preferably is nonionic in nature. Nonionic spin finishes are commercially available, and a preferred one is Dispersol VL. Suitably usable is Nopcostat 2152P, which is thought to be a modified coconut fatty acid ester. Finishes containing mineral oil act as a plasticizer and can increase dye uptake rate at the fiber surface. A water-dispersible or water-soluble finish such as Dispersol VL is preferred. Finishing operations can optionally be performed on the fibers before dyeing. For example, the fibers can be texturized by mechanically crimping or forming, such as described in *Textile Fibers, Dyes, Finishes, and Processes: A Concise Guide*, Howard L. Needles, Noyes Publications, 1986, pp. 17-20.

It has been found desirable in some applications to blend a polyamide, such as nylon 6 or nylon 6,6, into a first composition (a polypropylene and ethylene copolymer composition) to further enhance the first composition without sacrificing

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the desired spinning or dyeing properties of the fiber. The addition of polyamide forms a second composition (e.g., a polypropylene/copolymer/nylon 6 composition) with improved flammability, improved tenacity and improved resiliency compared to the first composition, even to a point that the modified fiber is more resilient than polypropylene alone. The added polyamide is by weight about 1 to 20%, and preferably 5 to 15%, the weight of the first composition. When a nylon component is added, the ethylene copolymer may be reduced provided that the alkyl acrylate component does not drop below an amount sufficient to keep the otherwise immiscible polypropylene and polyamide from separating (usually about 0.5% by weight). A preferred composition is about 1.4% alkyl acrylate component (approximately 7% ethylene copolymer) and 15% nylon 6, with the remainder (approximately 93%) polypropylene. For this one preferred composition, the alternatively expressed phr values are 100 phr polypropylene, 7.5 phr ethylene copolymer, and 16.1 phr nylon.

In using a composition of the polypropylene and ethylene alkyl acrylate copolymer (and optionally with polyester/copolyester and/or hydrophilic modifier), it is important that the polypropylene and ethylene alkyl acrylate copolymer be uniformly incorporated prior to forming the composition into a shaped article. The combination may be only a uniform blend, but preferably, and in accordance with this invention, it is a composition in which at least a portion of the ethylene alkyl acrylate is grafted onto the polypropylene. Blending and/or grafting can be accomplished in a separate step prior to forming, or the blending and/or grafting and extrusion can be carried out in the same operation if the extruder has a suitable mixing section. Poor blending and/or grafting can result in uneven dyeing even if the remaining steps of dyeing procedure are properly conducted.

The grafting of ethylene alkyl acrylate copolymer to polyolefin polymer, preferably isotactic polypropylene, for use in this invention is accomplished by subjecting the ethylene alkyl acrylate copolymer to co-graft polymerization in the presence of the polyolefin polymer. The graft polymerization method is not critical and the graft polymerization can be effected according to conventional methods employing organic free radical initiators. The polymerization conditions may be those known to the art. The organic radical-generating agent used in this invention includes:

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- 2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3,
2,5-dimethyl-2,5-di(t-butylperoxy)hexane,
1,3-bis(t-butylperoxyisopropyl)benzene,
2,2-bis(t-butylperoxy)-p-diisopropylbenzene,
5 dicumyl peroxide,
di-t-butyl peroxide, t-butyl benzoate,
1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane,
2,4-dichlorobenzoyl peroxide,
benzoyl peroxide,
10 azobisisobutyronitrile, and the like.

Preferred are:

- 2,5-dimethyl-2,5-di(t-butylperoxy)hexene-3,
1,3-bis(t-butylperoxyisopropyl)benzene, and
2,2-bis(t-butylperoxy)-p-diisopropylbenzene.

- 15 The thermoplastic resin composition of this invention can be obtained by adding 0.01 to 0.3 parts by weight, preferably 0.05 to 0.2 parts by weight, of an organic radical-generating agent to 100 parts by weight of a mixture consisting of 99 to 85% by weight, preferably 96 to 90% by weight, of polypropylene, and 2 to 13% by weight, preferably 4 to 10% by weight, of an ethylene alkyl acrylate copolymer,
20 and then subjecting the resulting mixture to thermal treatment in a mixer (e.g., a Banbury mixer, a kneader) or an extruder at 170° to 300°C, preferably 180° to 250°C, for 0.2 to 30 minutes, preferably 0.5 to 20 minutes. Fiber grade polyester may subsequently be introduced up to 15% by weight, preferably about 3 to 5% by weight, of the entire matrix, in which case the polypropylene percent would be
25 decreased by the weight percent of added polyester.

- When polyester is not incorporated into the matrix, the composition comprises about 99 to 85% by weight polyolefin, preferably polypropylene, and about 1 to 13% by weight the polar group material, preferably EMA. The alkyl acrylate in the composition is about 3% by weight or less, and the maximum amount of ethylene is
30 about 10% by weight. If a hydrophilic modifier as discussed above is utilized in the composition, it has a maximum contribution of 2% by weight to the overall matrix.

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When polyester is incorporated into the composition, the amount of polar group material and hydrophilic modifier need not change. The added 0.1 to 15% by weight polyester to the total composition will thus decrease the range of polyolefin to about 99 to 70% by weight. In the matrix of only polyolefin and polyester, the polyolefin comprises from 99.9 to 82% by weight, and the polyester comprises 0.1 to 18% by weight. Maleic anhydride or acrylic acid may be substituted for EMA as the polar group material when polyester is included in the composition, although the weight percent of these alternative and less preferred polar materials will be less than the weight percent of EMA.

One embodiment of this invention deals with the synergistic phenomena among polypropylene, polyester or copolyester, ethylene methyl acrylate (or maleic anhydride or acrylic acid), and preferably a hydrophilic modifier comprising a monoglyceride and a salt of a linear alkyl. Polyolefin-type polymers are the most challenging fibers to wet using conventional fiber production techniques. Polypropylene practically is a nonpolar polyolefin polymer with a very low surface energy. It has been reported that the surface energy of polypropylene is a 28.7 dynes/cm with 26.0 and 2.7 dynes/cm dispersive and polar fractions, respectively.

Polypropylene can be modified with EMA at a certain level to enable the polyolefin fibers to be reliably dyed with disperse dyes. However, the introduction of polar groups does not impart any "wetable" or "dyeable" characteristics. Similarly, both acrylic acid and maleic anhydride modified products also do not yield a wettable polymer or fiber. Commercial materials, such as the Polybond™ material from Uniroyal Chemical Company, Inc., combine functional monomers such as acrylic acid or maleic anhydride with polyolefin, and thereby form chemically grafted polyolefin copolymers. This chemically grafted polyolefin copolymer, when combined with polypropylene, similarly does not produce a wettable fiber.

When a preferred hydrophilic modifier such as disclosed herein is used in conjunction with polar substrates, such as EMA or Polybond™, the wettability of the polyolefin improves dramatically, as measured by contact angle. In some applications, this increased wettability is beneficial to obtaining desired dyeability characteristics.

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A preferred modifier is a combination of nonionic and anionic structures. The nonionic structure may be a monoglyceride with a melting point of approximately 66°C and a boiling point of approximately 260°C. Glycerol monostearate ("GMS") is the presently preferred monoglyceride. This nonionic structure is highly distilled, with a monoglyceride content in excess of 95% by weight. In some applications, a monoglyceride without an anionic structure may be a suitable modifier. The minor component has an anionic structure and is a potassium salt linear alkyl (C₁₆ to C₁₈) phosphate. The preferred ratio of these two components varies depending on the application, although the nonionic structure preferably is from 50 to 90% by weight of the modifier. A 80:20 ratio by weight of the nonionic and anionic structure is preferred. Other preferred hydrophilic modifiers are polypropylene glycol polyoxyethylates and fatty alcohol polyoxyethylates. Other hydrophilic modifiers may include alkyl phenol polyoxyethylates, fatty acid polyoxyethylates, and fatty acid amide polyoxyethylates.

A preferred hydrophilic modifier is Product No. 5808, available from G.R. Goulston and Company in Monroe, North Carolina. This compound (hereafter "5808 Modifier") consists of a mixture of a food grade emulsifier, such as mono and diglycerides of edible fats and oils, and a salt of a linear alkyl phosphate. The push to migrate or exude towards the surface comes from the highly distilled (>90%) monoglyceride, which by itself does not impart the surface wettability. Accordingly, it is beneficial to melt/fuse the monoglyceride with the long chain hydrocarbons having the hydrophilic group component so as to realize the significant impact on surface wettability. This melt/fuse operation may be performed by a prilling process or a pastillizing process so that heat transfer takes place in a manner that will not degrade the monoglyceride.

Olefin polymers do not disperse particularly well in linear polyester or copolyester. While an olefin component in theory might be incorporated into the polyester at the polymerization stage, this would be highly disadvantageous because of the requirement to provide an injection facility for the added olefin or polyolefin component. Moreover, polypropylene will degrade dramatically during the polyester polymerization process. If the polyester were added during the polymerization of polyolefin, the entire process would be poisoned due to polar moiety.

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The dispersibility of linear polyester into the olefinic polymers can be significantly improved by the incorporation of a polar group material, e.g., EMA, which can be enhanced further by a hydrophilic modifier. The linear polyester may be produced by condensing one or more dicarboxylic acids or a lower alkyl diester
5 (e.g., terephthalic acid, isophthalic acid, phthalic acid, 2,5-; 2,6-; or 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic acid, azelaic acid, bibenzoic acid, and hexahydroterephthalic acid or bis-p-carboxyphenoxyethane) with one or more glycols (e.g., ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, and 1,4-cyclohexanedimethanol). The preferred polyester is polyethylene
10 terephthalate, and a fiber grade polyester will have an intrinsic viscosity of about 0.64.

The polyester may be a copolymer containing a mixed hydroxylic acid and/or ester forming acidic groups and may be a block copolymer formed from different polyesters. The copolyester may contain polymeric segments having a glass-transition
15 temperature of less than 0°C so that the polyester is internally plasticized. The polymer used for the polymeric segment should be capable of undergoing polycondensation with the segments of the polyester through reactive end groups, and as hydroxyl or carboxyl groups, or being linked to polyester segments. Suitable polymeric segments are polyethylene glycol and polytetramethylene glycol, with the
20 polyester segment typically being polyethylene terephthalate or polybutyl terephthalate.

This invention thus reduces or eliminates the drawbacks due to poor dispersability of a polyolefin resin and a polyester resin in each other. A composition and process capable of providing continuous filaments or fibers is disclosed that
25 significantly improves the dyeability of a polyolefin composition.

As known in the art, various specialized techniques have been developed for application of disperse dyes to fibers. Unless the dyeing is carried out at 100°C or above, the rate of dyeing is slow. Dyeing with disperse dyes from aqueous solutions at 120-130°C to achieve rapid dyeings requires the use of closed high-pressure
30 equipment. Jet dyeing has been introduced that permits high-temperature dyeing and impingement of the dye onto the moving fabric through use of a venturi jet system. Carriers permit faster dyeing at atmospheric pressure and below 100°C. Carriers are

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usually organic compounds that can be emulsified in water and that have affinity for the fiber polymer. The carriers penetrate the polymer, often swelling the fiber, and aid passage of the disperse dye across the dye solution fiber interface into the fiber. Suitable carriers include aromatic hydrocarbons such as diphenyl and
5 methylnaphthalene, phenolics such as o- and p-phenylphenol, halogenated aromatics such as the di- and trichloro-benzenes, aromatic esters including methyl salicylate, butyl benzoate, diethylphthalate, and benzaldehydes. Carriers must be removed after dyeing.

A preferred swelling agent is of the type disclosed in U.S. Patent No.
10 5,358,537 to Shaw Industries, Inc. A polypropylene-based compound as disclosed herein accordingly may also include a swelling agent, such as n-cyclohexyl-2-pyrrolidone, diethylene glycol, or n-octyl-2-pyrrolidone. A mixture of n-cyclohexyl-2-pyrrolidone and diethylene glycol may be preferred. The mixture may also include an amphoteric agent, such as Wacogen NH600N, Chemcogen 132-N, or combinations
15 thereof to act as a wetting agent or dye compatibilizer, thereby significantly enhancing dyeing characteristics. For space dyeing and printing applications, the dye mixture preferably is in the form of a paste to allow for the selective placement of the mixture on the yarn, fabric, or carpet. For such applications, the viscosity of the mixture may be adjusted from about 800 to about 3,000 centipoise (at 80°F as measured by
20 the Brookfield Viscometer with a No. 3 spindle). A selected thickener from group consisting of guar gum, gum arabic, modified cellulose, locust bean gum, xanthene gum and combinations thereof may be used to obtain the desired viscosity. A dye mixture comprising a disperse dye and the additives such as described above may be applied to the polypropylene fibers. A dry heat may then be applied to the fibers and
25 the dye mixture at a temperature of from 95°C to about 110°C for time sufficient to effect dispersion of at least a portion of the disperse dye into the polypropylene fibers. Generally from 1 minute to 10 minutes of exposure to dry heat should achieve the desired dispersion. The residual dye is then removed from the fibers.

A disperse dye mixture may thus be applied to the polypropylene fibers in
30 various ways. The dye mixture may be applied intermittently along the length of yarn formed from fibers using various well known techniques to create a desired effect. One suitable method of dyeing fibers may be referred to as the "knit-deknit"

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dyeing technique. According to this method, the fibers are formed into a yarn which in turn is knit, typically into a tubing configuration. The dye mixture is then intermittently applied to the knit tubing. After dyeing, the tubing is unraveled and the yarn thus has an intermittent pattern. According to an alternative printing method,
5 the fibers are first formed into yarn which is then woven or knitted into fabric, or is tufted into the carpet. A conventional flat screen printing machine, such as sold by Peter Zimmer, Inc., may be used for applying the dye mixture to the fabric or carpet.

Continuous dyeing is carried out on a dyeing range where fabric or carpet is continuously passed through a dye solution of sufficient length to achieve initial dye
10 penetration. Some disperse dyes may be sublimated under heat and partial vacuum into polymer fiber by methods known in the art. Printing of polyolefin compositions made in accordance with our invention can be accomplished with disperse dyes by heat transfer printing under pressure with sufficient heating to cause diffusion of disperse dyes into the polyolefin. Block, flat screen, and heat transfer batch
15 processes, and engraved roller and rotary screen printing continuous processes may be used. Different dye solutions may be jet-sprayed in programmed sequence onto fabric or carpet made of the compositions of this invention as the fabric passes under the jets to form patterns. Dye solution may be metered and broken or cut into a pattern of drops that are allowed to drop on a dyed carpet passing underneath to give
20 a diffuse overdyed pattern on the carpet. Competitive dyeing of polyolefins is useful when dyeing styled carpets consisting of several different fibers such as nylon, polyester, etc., and a polyolefin. Different styling effects can be produced by controlling shade depth on each type of fiber present. Acid, disperse and premetallized dyes, or combinations thereof, depending upon the fibers present, can
25 be employed to obtain styling effects. Also, styling effects obtained from a fiber combination can be achieved by making a fabric or carpet face from polyolefin yarns containing varying amounts of ethylene alkyl acrylate copolymer. Just as tweed effects can be produced in a nylon carpet by tufting with nylon fibers containing different levels of amine ends, so too can these styled, tweed effects be produced in
30 a polyolefin fiber by controlling the concentration of ethylene alkylacrylate dye sites. Print dyeing, space dyeing, and continuous dyeing can be carried out with fabrics made from such yarns.

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The invention can be further understood by referring to the following examples in which parts and percentages are by weight unless otherwise indicated. In Examples 4, 5 and 6, polyester was added to the polypropylene composition.

Example 4

5 A polypropylene alloy composition containing 82.5% by weight of a commercial fiber grade of isotactic polypropylene as per Example 1, and 7% by weight of a copolymer of ethylene methacrylate along with 5808 Modifier (0.5% by weight) was prepared by first dry mixing the polymers and then melt blending the mix in a 40 mm Berstorff extruder at 246°C. The ethylene copolymer contained 20%
10 by weight of the methacrylate comonomer and had a melt index of 18 (ASTM D-1238-89, 190°C, 2.16 lbs). The fiber grade polyester was blended in at 10% of the total matrix. The resulting homogeneous, compatible polymer blend was cut into nibs after water-quenching, which were then fed to a melt spinning apparatus, and 50-60 denier per filament fiber was spun at 260-265°C. A mineral-oil-based finish
15 containing anionic surfactants was applied to the fiber bundle after spinning, but before drawing. The fibers were drawn times three to give a final denier of 18-20 per filament. The physical properties of specimens of the fibers so prepared were tested, and the test results are set forth in Table II. Specimens of the fibers were knitted on a knitting machine to produce a tubular knit fabric. Samples of the fibers
20 were also tested for wetting characteristics.

Example 5

 A polypropylene graft composition containing 82.5% by weight of a commercial fiber grade of isotactic polypropylene as per Example 2, and 7% by weight of a grafted copolymer of ethylene methacrylate (and containing thermal,
25 oxidative, and ultraviolet light stabilizers) was prepared by first dry mixing the polymers along with 0.5% by weight of the 5808 Modifier. This mixture was combined with the fiber grade copolyester at 10% by weight of the total matrix. The resulting mixture was melt blended in a 40 mm Berstorff extruder at 246°C in the presence of sufficient free radical initiator peroxide per Example 2. The ethylene
30 copolymer contained 20% by weight of the methacrylate comonomer and had a melt

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index of 18. The resulting homogeneous, compatible polymer blend was cut into nibs after water-quenching, which were then fed to a melt spinning apparatus, and 50-60 denier per filament fiber was spun at 260-265°C. A mineral-oil-based finish containing anionic surfactants was applied to the fiber bundle after spinning, but before drawing. The fibers were drawn times three to give a final denier of 18-20 per filament. The physical properties of specimens of the fibers so prepared were tested, and the test results are set forth in Table II. Specimens of the fibers were knitted on a knitting machine to produce a tubular knit fabric. Samples of the fabric were also tested for wetting characteristics.

TABLE II

Physical Properties	(Unmodified homopolymer)	<u>Example 4</u> (Alloy Modified PP)	<u>Example 5</u> (Grafted Modified PP)
Denier (gms/9000 meters)	1,450	1,500	1,470
Tensile (gms/den)	2.5	2.0	2.2
Elongation (%)	39.0	65.0	70.0

Example 6

A polypropylene combination alloy and graft composition containing 82.5% by weight of a commercial fiber grade of isotactic polypropylene having a melt index in the range of 8-12 (ASTM D-1238-89, 230°C, 2.16 lbs) (and containing thermal, oxidative, and ultraviolet light stabilizers) and 7% by weight of an alloyed and grafted copolymer of ethylene methylacrylate was prepared by first dry mixing the polymers along with a 5808 Modifier (0.5% by weight), and then melt blending the mix with fiber grade copolyester at 10% of the total matrix in a 40 mm Berstorff extruder at 246°C in the presence of sufficient free radical initiator peroxide as per Example 2. The ethylene copolymer contains 20% by weight of the methylacrylate comonomer

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and had a melt index of 18 (ASTM D-1238-89, 190°C, 2.16 lbs). The resulting homogeneous, compatible polymer blend was cut into ribs after water-quenching, which were then fed to a melt spinning apparatus, and 50 to 60 denier per filament fiber was spun at 260 to 265°C. A mineral-oil-based finish containing anionic surfactants was applied to the fiber bundle after spinning, but before drawing. The fibers were drawn times three to give a final denier of 18 to 20 per filament. The physical properties of specimens of the fibers so prepared were tested, and the test results were about the same as those obtained with the fibers of Example 5. Specimens of the fibers were knitted on a knitting machine to produce a tubular knit fabric. Samples of the fibers were also tested for dyeing and wetting characteristics, according to the dyeing procedure of Example 1.

While the prior art teaches the existence of polypropylene incorporated (by grafting or blending) with ethylene-alkyl acrylate copolymers, the above examples illustrate that, in only certain limited amounts, a particular ethylene copolymer with a proper combination with polyester and hydrophilic modifier has the surprising ability of making a commercially acceptable, spinnable textile fiber of polypropylene that can accept disperse dyes sufficient to produce a deeply colored fiber with superior physical properties.

Those skilled in the fiber-making art have long believed that any acrylate additive produces a resin composition that cannot be spun at modern high-speed production without separation of the components. Further, the addition of many additives, including acrylates and acetates, imparts a disagreeable feel and smell to the finished fiber goods, partially as a result of degradation during the spinning and drawing process. Fiber manufacture typically imparts terrific shear forces to a polymer composition and "draw down" ratios of 20-100:1, which makes fiber-forming polymers very intolerant of many additives routinely employed in compositions having other uses. Any discontinuity or lack of uniformity in a polymer composition can result in a break when the fiber is stretched or drawn down to its final, often very thin, diameter. As a consequence, those skilled in the fiber-making art have generally not looked to compositions for other end uses as acceptable in fiber applications, particularly in areas where historical experience suggests unacceptability. The critical nature of the invention is appreciated in that a 0.2 to 3.0% by weight limitation on

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alkyl acrylate component in the composition, in combination with a less than about 10% by weight ethylene content attributed from the alkyl acrylate copolymer, is required to produce the desired results sufficient to achieve commercial acceptability. The hydrophilic modifier provides additional compatibilization to bridge polyester with polypropylene.

The ethylene copolymer is incorporated into the polypropylene by either grafting or physical blending. Those skilled in the fiber-making art have recognized that polypropylene/EVA compositions cannot produce a spinnable fiber under modern fiber-making conditions, but instead this composition very quickly degrades to produce noxious amounts of acetic acid. No other known copolymers are believed to produce commercially acceptable dyeable fibers in combination with polypropylene.

A series of samples was made as described in Example 5 and was evaluated with a series of disperse dyes according to the dye procedure described earlier. The results are set forth in Table III. Light fastness and crock fastness tests were also performed on yarns at 2-20 deniers per filament. Comparable results would be expected for both the Example 4 and Example 6 samples.

Table III

Dye Exhaustion				
Disperse Dyes (3% Concentration)	Light Fastness Xenon Arc (AATCC 16E-40 hrs.)	Crock Fastness (AATCC 8-1985)		Exhaust/ Yield
		Dry	Wet	
Disperse Yellow 54	5	5	5	5
Disperse Yellow 86	5	4-5	4-5	5
Disperse Blue 35	5	5	5	5
Disperse Blue 87	5	5	4-5	5
Disperse Blue 291	5	5	4-5	5
Disperse Blue 60	5	4	4	5

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Disperse Red 60	5	4	4	5
Disperse Orange 25	5	5	5	5

Dye exhaust, set forth in the last column, has been used as the basis for identifying dyes suitable for the polymer. Of all the workhorse dyes that are known to exist, most disperse dyes should produce acceptable results if polyester is added to the polypropylene mixture. The most important criteria for dye selection, in contemporary times, are dye exhaust and fastness retention. It is important that the substrate in a woven, tufted, knitted, or nonwoven product readily pick up the dye from the bath and retain it, thereby reducing environmental waste and improving economic utility of the expensive dye. Hardly any differences appear to exist when these criteria are used to evaluate dye performance between 100% polyester fabric and enhanced polyolefin fabric.

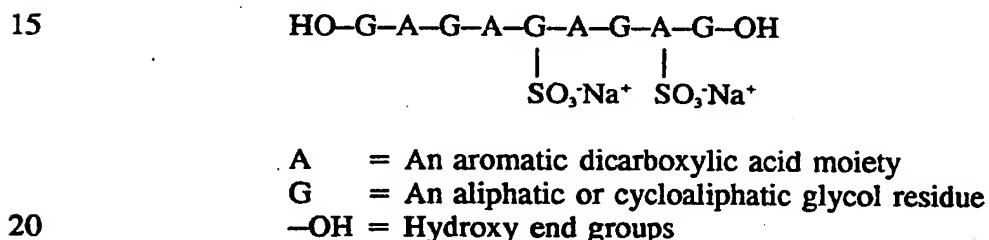
While those skilled in the fiber-making art have recognized that polyester fiber is well accepted for disperse dye applications, it was not recognized that polyester at a very minute level (approximately 0.1% by weight of the polyolefin resin matrix) creates voids that tremendously enhance the dye uptake. The processibility of this composition is also significantly improved by adding a hydrophilic modifier. Though not bound by any theory, it is believed that increased wettability due to the combined nature of polarity and hydrophilicity (the polar group material combined with monoglyceride and linear alkyl phosphate) and morphological changes caused by the addition of polyester causes the disperse dyes to diffuse into the fiber very rapidly (i.e., high exhaust) and tend to stay (i.e., increased light fastness characteristics). The above composition is much more dyeable than prior art polypropylene-based materials. It is speculated that the combination of increased dispersive and polar functions far exceeds the surface energy that is critical for adequate wetting to occur on polyolefin surfaces. Neither a polar material nor a hydrophilic modifier on its own is capable of imparting such a highly desirable characteristic that produces good spreading and therefore even dyeing. With a lesser barrier to overcome, the above material therefore is comparatively easy to dye compared to conventionally modified polypropylene materials.

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Hydrogen bonding of the dyestuff molecule to the carbonyl oxygen of the ester grouping in methyl acrylate is believed to be the attachment mode of the disperse dyestuff. The disperse dyestuff exhibits excellent retention, indicating strong chemical affinity between the functionality in the ester group and dyestuff. The penetration of dye molecules is facilitated by creating a hydrophilic structure with voids created by the incorporation of polyester.

To enhance the dyeability characteristic, especially with cationic dyes, several attempts were made to introduce a sulfonic group on a polymer. A sulfonic group on a polymer should improve dyeing, especially utilizing cationic dyes instead of disperse dyes. This invention discloses a method of causing sulfophthalic acid to react with an olefin (or polyolefin) or with an alkyl acrylate copolymer.

Sulfopolyesters were made by the polycondensation reaction of the selected dicarboxylic acids (A's) and glycols (G's) to produce a linear structure shown below in a simplified form:



The polycondensation reaction, in which a carboxyl group (-COOH) reacts with a hydroxyl group (-OH) to form ester linkages, is carried out at high temperatures (275°C to 290°C) and low pressure (<1 torr) to produce number-average molecular weights in the 10,000 to 15,000 range. The thermal stability of a polymer formed under such extreme conditions is adequate for most fiber spinning process applications. Adding a sulfonic group to the polyester is much easier than adding a sulfonic group to polypropylene. It may be possible, however, to produce a sulfonated hydrophilic modifier.

As indicated in the above structure, some of the aromatic dicarboxylic acid units have sodiosulfo (-SO₃Na⁺) substituents attached. The sulfopolyesters feature of this invention requires more ionic groups in order to make the entire fiber structure

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more acceptable to cationic dyes. The hydrophilic nature of these ionic groups also imparts improved disperse dyeability. Several basic dyes were attempted on a fiber composed of polypropylene, alkyl acrylate copolymer, and sulfopolyester with and without additional hydrophilic modifier.

5 Basic dyes have been used extensively for dyeing silk, cellulose acetate, and polyacrylonitrile (acrylic or modified acrylic) fibers. The positively charged colored ion of the basic dye, the cation, is attracted strongly by the negatively charged ions in the fiber. Fibers dyed with basic dyes usually exhibit good light and wash fastness. As a class, basic dyes have a high color value and are characterized by
10 brilliant shades. Basic dyes are thus well suited for application to fibers composed of negatively charged polymer molecules. Since basic or ionic dyes contain positively charged ions, bonds can be easily formed between the cation of these dyes and an ionic sites in the fibers. At the conclusion of the dye cycle, the dye cations are almost completely absorbed or complete exhausted by the fiber.

15 Based upon this understanding, a sulfonated group was introduced to the polyester component of the polypropylene mixture by a grafting technique, as described above. Tests were conducted using basic workhorse dyes, including Basic Blue-41 and Basic Red-46. Each of these dyes, when used in conjunction with a polypropylene mixture including a sulfopolyester as described above, yielded brilliant
20 shades on fibers. A grafting technique is preferably employed to include the sulfonated group on the polyester.

 From the above examples, it may be understood that the addition of both polar group material and the hydrophilic modifier to a polypropylene-based material will result in a material that is hydrophilic and thus "wetable." The polar group material
25 may be an EMA material as described above, or may be either an acrylic acid comprising about 0.1 to 2% by weight of the polypropylene, or a maleic anhydride comprising about 0.1 to 10%, and preferably 0.1 to 2%, by weight of the polypropylene. The hydrophilic modifier may be either a nonionic or anionic material and may be used in compositions wherein the hydrophilic modifier is present
30 in the amount of between 0.1 and 2%, and preferably between 0.4 and 1.0%, of the weight of the polypropylene and polar group material. The addition of polyester thus is facilitated by this compatibilizing characteristic.

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The polymers as described above thus have significantly improved hydrophilic characteristics that enable the polymers to be formed into fibers suitable for fabrics or into injection molded films. These polymers provide improved dyeability and particularly make the polymer dyeable with a broad range of disperse dyes. This increased dyeability feature is of great importance because certain disperse dye molecules are too large to diffuse into the fiber core of prior art polypropylene fibers, but these same molecules may penetrate into the improved polypropylene fibers of this invention. Dye selection therefore becomes less complex, and the final shade of the dyed product is brighter, deeper, and sharper than prior art compositions. This wettability characteristic also should provide excellent exhaustion for the dyed products since the dye molecules, once in place in a fiber, should tend to stay in place. Improved wash fastness and crock fastness results may thus be expected, and the product should be both wettable and dyeable for various applications.

A hydrophilic dyeable and wettable polymer provides highly desirable material features, such as permanency, wickability, and extra comfort. These attributes are highly desired in product applications such as diapers, adult incontinence products, and sanitary napkins, where a nonwoven web comes in contact with the body or entry point for any fluid penetration.

The composition of this invention may be used for forming both a highly wettable and dyeable polyolefin, as well as a resilient polyolefin. The composition is particularly suitable for forming improved polypropylene-based polyolefin. To substantially increase acceptance of polypropylene as a suitable replacement for various applications as discussed above requires increased dyeability and increased wettability. Moreover, the polypropylene composition of this invention may be easily formed as a fiber that is spinnable and ideally may be formed into a fabric sheet including nonwoven fibers.

Polypropylene and polyester are generally not considered compatible materials for forming continuous fibers due to the significant difference in their softening and melting temperatures. The ethylene methyl acrylate acts as a compatibilizer to allow the polyester to adhere to the polypropylene. This compatibilization is enhanced by the inclusion of the hydrophilic modifier as discussed above. This modifier also

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enhances the processibility of the composition to form spinnable fibers and imparts a desired resiliency and softness to the fabric formed by these fibers.

While the techniques of the present invention are particularly well suited for increasing both the dyeability and the wettability characteristics of polypropylene, it should be understood that the selected polar group material, such as an ethylene copolymer including alkyl acrylate as described above, in combination with a hydrophilic modifier as described above, may be used to substantially increase the wettability characteristics of other polymeric materials, such as polyester, nylon, and acetate, all of which may be used to form fibers. Those skilled in the art will also appreciate that fibers made of a polyolefin material as disclosed herein may be used for various woven or nonwoven applications to form either fabrics or mats. The fibers may also be combined with other common stock materials, such as pulp or paper stock, to form a desired wettable and breathable fabric or mat. As previously explained, the concept of the present invention may also be used for form materials such as fibrillated films that do not include fibers.

Various modifications to the modified polypropylene fibers and to the techniques described herein for forming and dyeing such fibers should be apparent from the above description of those preferred embodiments. Although the invention has thus been described in detail for these embodiments, it should be understood that this explanation is for illustration and that the invention is not limited to these embodiments. Alternative fibers and forming and dyeing techniques will thus be apparent to those skilled in the art in view of this disclosure, and such alternative fibers and techniques may be performed without departing from the spirit of the invention, which is defined by the claims.

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What is claimed is:

1. A process for dyeing polypropylene based fibers, comprising:
 - (a) forming into a fiber a composition of about 99 to 70% by weight of a polypropylene and an ethylene copolymer comprising about 70 to 82% by weight
5 ethylene and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl has one to four carbon atoms, said alkyl acrylate present in the composition in an amount between 0.2 to 3.0% by weight of the sum of the polypropylene and ethylene
10 copolymer; and the ethylene from said ethylene copolymer present in the composition in an amount less than about 10% by weight of the sum of the polypropylene and ethylene copolymer; and
(b) exposing the fiber to a dye.
2. The process of Claim 1 wherein the alkyl acrylate is present in an amount between 0.5 to 2.4% by weight.
3. The process of Claim 1 wherein at least a portion of the ethylene
15 copolymer is grafted onto said polypropylene.
4. The process of Claim 1 wherein the ethylene copolymer is melt blended into the polypropylene.
5. The process of Claim 1 wherein the ethylene copolymer is ethylene methyl acrylate.
- 20 6. The process of Claim 1 wherein the ethylene copolymer is ethylene ethyl acrylate.
7. A colored polyolefin fiber, comprising:
 - (a) about 97 to 70% by weight of a polypropylene;
 - (b) an ethylene copolymer comprising about 70 to 82% by weight ethylene
25 and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl acrylate has one to four carbon atoms, said alkyl acrylate being present in an amount between 0.2%

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to 3.0% by weight, and wherein the ethylene from said ethylene copolymer is present in an amount less than about 10% by weight; and

(c) an effective amount of a dye to produce a colored fiber.

8. The fiber of Claim 7 wherein the ethylene copolymer is ethylene
5 methyl acrylate.

9. The fiber of Claim 7 wherein said alkyl acrylate is present in an amount of 0.5 to 2.4% by weight.

10. The fiber of Claim 7, further comprising:
a hydrophilic modifier comprising at least 50% by weight a monoglyceride and
10 a salt of a linear alkyl, the hydrophilic modifier being in an amount by weight of about 0.1 to 2.0%.

11. The fiber of Claim 7 wherein at least a portion of the ethylene copolymer is grafted onto said polypropylene.

12. The fiber of Claim 7 wherein the ethylene copolymer is ethylene ethyl
15 acrylate.

13. A process for forming a dyeable polyolefin composition, comprising:
(a) forming a composition including about 99 to 70% by weight polyolefin, 0.1 to 15% by weight polyester, and a polar group material, the polar group material selected from a group consisting of (1) an ethylene copolymer, the ethylene
20 copolymer comprising about 70 to 82% by weight ethylene and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl has one to four carbon atoms, the alkyl acrylate present in the composition in an amount of from 0.2 to 3.0% by weight of the composition, (2) a maleic anhydride comprising about 0.1 to 10% by weight of the composition, and (3) an acrylic acid comprising about 0.1 to 2.0% by weight of
25 the composition; and

(b) exposing the composition to a dye.

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14. The process of Claim 13, wherein the polyester comprises from 1 to 10% by weight of the composition.

15. The process of Claim 13, further comprising:
a hydrophilic modifier comprising at least 50% by weight a monoglyceride and
5 a salt of a linear alkyl, the hydrophilic modifier being in an amount by weight of about 0.1 to 2% of the composition.

16. The process of Claim 15, wherein the salt is a salt of a linear alkyl phosphate having a hydrocarbon chain length of from 14 to 18 carbons, and the monoglyceride and the salt of a linear alkyl phosphate are fused.

10 17. The process of Claim 13, further comprising:
attaching a sulfonic group to the polyester; and
step (b) comprises exposing the composition to a cationic dye.

15 18. The process of Claim 13, further comprising:
providing a dye mixture comprising a disperse dye and a swelling agent; and
step (b) comprises subjecting the composition and the dye mixture to a
temperature of from about 95°C to about 110°C to disperse the disperse dye into the
composition.

19. The process of Claim 13, wherein the polar group material is an ethylene copolymer.

20 20. The process of Claim 19, wherein the ethylene copolymer is ethylene methyl acrylate.

21. The process of Claim 13, wherein the polar group material is an ethylene copolymer and the ethylene copolymer is present in an amount of from 2 to 13% by weight of the composition.

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22. A polyolefin composition, comprising:
- (a) about 99 to 70% by weight polyolefin;
 - (b) 0.1 to 15% by weight polyester; and
 - (c) a selected amount of a polar group material selected from a group
- 5 consisting of (1) an ethylene copolymer comprising 70 to 82% and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl acrylate has 1 to 4 carbon atoms, the alkyl acrylate being present in an amount of from 0.2 to 3.0% by weight of the composition, (2) a maleic anhydride comprising about 0.1 to 10% by weight of the composition, and (3) an acrylic acid comprising about 0.1 to 2.0% by weight of the
- 10 composition.
23. The composition of Claim 22, wherein the polyester comprises from 1 to 10% by weight of the composition.
24. The composition of Claim 22, wherein the polar group material is ethylene copolymer and at least a portion of the ethylene copolymer is grafted onto
- 15 the polyolefin.
25. The composition of Claim 22, wherein the polar group material is ethylene copolymer and the alkyl acrylate is present in an amount of 0.5 to 2.4% by weight of the composition.
26. The composition of Claim 22, wherein the polar group material is an
- 20 ethylene copolymer and the ethylene copolymer is present in an amount of from 2 to 13% by weight of the composition.
27. The composition of Claim 22, further comprising:
- a hydrophilic modifier in an amount by weight of from 0.1 to 2.0% of the composition, the hydrophilic modifier comprising a monoglyceride and a salt of a
- 25 linear alkyl.

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28. The composition of Claim 27, wherein the hydrophilic modifier comprises a linear alkyl phosphate, the monoglyceride is glycerol monostearate, and the glycerol monostearate and the salt of a linear alkyl are fused.

29. A process for forming colored fibers from a polypropylene-based
5 composition, comprising:

- (a) combining polypropylene with an ethylene copolymer of about 70 to 82% by weight ethylene and about 30 to 18% by weight of an ethylene alkyl acrylate wherein the alkyl group has 1 to 4 carbon atoms to form a composition, the alkyl acrylate present in the composition in an amount of from 0.2 to 3.0% by weight of
10 the polypropylene;
- (b) adding a polyester by weight from 0.1 to 15% of the composition;
- (c) extruding the composition into fibers; and
- (d) exposing the fibers to a dye to color the fibers.

30. The process of Claim 29, further comprising:
15 the polypropylene being from 99 to 70% by weight of the composition; and grafting the ethylene copolymer onto the polypropylene prior to adding the polyester.

31. The process of Claim 29, wherein the polyester comprises from 1 to 10% by weight of the composition.

20 32. The process of Claim 29, further comprising:
a hydrophilic modifier comprising at least 50% by weight a monoglyceride and a salt of a linear alkyl, the hydrophilic modifier being in an amount by weight of about 0.1 to 2% of the composition.

25 33. The process of Claim 29, further comprising:
attaching a sulfonic group to the polyester; and
step (d) comprises exposing the fibers to a cationic dye.

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34. The process of Claim 29, further comprising:
providing a dye mixture comprising a disperse dye and a swelling agent; and
step (d) comprises subjecting the composition and the dye mixture to a
temperature of from about 95°C to about 110°C to disperse the disperse dye into the
5 composition.

35. A polypropylene-based fiber composition, comprising:
(a) about 99 to 70% by weight polypropylene;
(b) about 0.1 to 15% by weight polyester; and
(c) an ethylene copolymer comprising 70 to 82% and about 30 to 18% by
10 weight of an alkyl acrylate wherein the alkyl acrylate has 1 to 4 carbon atoms, said
alkyl acrylate being present in an amount of from 0.2 to 3.0% by weight of the
composition.

36. The composition of Claim 35, wherein the polyester comprises from
1 to 10% by weight of the composition.

15 37. The composition of Claim 35, wherein at least a portion of the ethylene
copolymer is grafted onto the polypropylene.

38. The composition of Claim 35, wherein the alkyl acrylate is present in
an amount of 0.5 to 2.4% by weight of the composition.

20 39. The composition of Claim 35, further comprising:
a hydrophilic modifier in an amount by weight of from 0.1 to 2.0% of the
composition, the hydrophilic modifier comprising a monoglyceride and a salt of a
linear alkyl.

40. The composition of Claim 39, wherein the hydrophilic modifier
comprises a linear alkyl phosphate.

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41. The composition of Claim 39, wherein the monoglyceride is glycerol monosterate, and the glycerol monosterate and the salt of a linear alkyl are fused.

42. A colored polypropylene fiber, comprising:

- (a) about 99 to 70% by weight polypropylene;
- 5 (b) about 0.1 to 15% by weight polyester; and
- (c) an ethylene copolymer comprising 70 to 80% and about 30 to 18% by weight of an alkyl acrylate wherein the alkyl acrylate has 1 to 4 carbon atoms, said alkyl acrylate being present in an amount of from 0.2 to 3.0 by weight;
- (d) a hydrophilic modifier in an amount by weight of from 0.1 to 2.0%,
- 10 (e) the hydrophilic modifier comprising a monoglyceride and a salt of a linear alkyl; and
- (e) an effective amount of dye to produce a colored fiber.

43. The fiber of Claim 42, wherein the polyester comprises from 1 to 10% by weight.

44. The fiber of Claim 42, wherein the alkyl acrylate is present in an
15 amount of 0.5 to 2.4% by weight.

45. The fiber of Claim 42, wherein the polyester includes a sulfonic group grafted thereon, and the dye is a cationic dye.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/06590

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : D06P 3/79; 3/54, 3/36; C08L 23/12

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/497, 922, 928; 525/64, 166, 168, 194, 227; 524/140, 317, 513, 523

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US, A, 3,433,573 (HOLLADAY) 18 March 1969, see Abstract, column 4, line 2, column 5, line 12.	1-9, 11, 12 ----- 13, 14, 18-26, 29-31, 34-38, 42-45
X	JP, B, 45-30945 (MITSUBISHI RAYON CO., LTD) 07 October 1970, see Abstract.	13, 14, 22, 23
X	JP, B, 43-6795 (CHISSO CORP.) 13 March 1968, see Abstract.	13, 14, 22, 23
Y	US, A, 3,419,638 (FUZEK) 31 December 1968, see claim 1.	13, 14, 18-26, 29-31, 34-38, 42-45

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* *A* *E* *L* *O* *P*	Special categories of cited documents: document defining the general state of the art which is not considered to be part of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	*T* *X* *Y* *A*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search

28 JUNE 1995

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09 AUG 1995

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/06590

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,431,322 (CALDWELL) 04 March 1969, see claim 1.	13, 14, 18-26, 29-31, 34-38, 42-45
A	GB, A, 902,809 (SPENCER CHEMICAL COMPANY) 09 August 1962, see examples.	1-9, 11, 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/06590

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

8/497, 922, 928; 525/64, 166, 168, 194, 227; 524/140, 317, 513, 523

Form PCT/ISA/210 (extra sheet)(July 1992)★

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